

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 285 915 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**26.02.2003 Bulletin 2003/09**

(51) Int Cl.7: **C07D 301/12**

(21) Application number: **01119565.8**

(22) Date of filing: **16.08.2001**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**  
Designated Extension States:  
**AL LT LV MK RO SI**

(71) Applicants:  
• **Degussa AG**  
**40474 Düsseldorf (DE)**  
• **Uhde GmbH**  
**44141 Dortmund (DE)**

(72) Inventors:  
• **Hofen, Willi**  
**63517 Rodenbach (DE)**  
• **Thiele, Georg Dr.**  
**63450 Hanau (DE)**

(74) Representative:  
**Sternagel, Fleischer, Godemeyer & Partner**  
**Patentanwälte**  
**Braunsberger Feld 29**  
**51429 Bergisch Gladbach (DE)**

(54) **Continuous process to make epoxide from olefins and hydrogen peroxide**

(57) The invention described herein relates to a process for the catalytic epoxidation of olefins with hydrogen peroxide in a continuous flow reaction system, wherein the reaction mixture comprising at least one liquid phase is passed through a fixed catalyst bed positioned

between parallel heat exchange plates and the reaction heat is at least partially removed during the course of the reaction by passing a cooling medium through the heat exchange plates.

**EP 1 285 915 A1**

**BEST AVAILABLE COPY**

## Description

### Prior Art

[0001] From EP-A 100 119 it is known that olefins can be converted by hydrogen peroxide into olefin oxides if a titanium-containing zeolite is used as catalyst.

[0002] Unreacted hydrogen peroxide cannot be recovered economically from the epoxidation reaction mixture. Furthermore, unreacted hydrogen peroxide involves additional effort and expenditure in the working up of the reaction mixture. The epoxidation of propene is therefore preferably carried out with an excess of propene and up to a high hydrogen peroxide conversion. In order to achieve a high hydrogen peroxide conversion it is advantageous to use a continuous flow reaction system. Such a reaction system may comprise either one or more flow reactors or an arrangement of two or more mixing reactors connected in series. Examples of mixing reactors are stirred tank reactors, recycle reactors, fluidized bed reactors and fixed bed reactors with recycling of the liquid phase.

[0003] In order to achieve a high reaction rate a high propene concentration in the liquid phase is necessary. The reaction is therefore preferably carried out under a propene atmosphere at elevated pressure with the effect that a multiphase reaction system is in general present.

[0004] Furthermore the epoxidation of olefins with hydrogen peroxide is like most oxidation reactions highly exothermic. Thus precautions have to be taken to ensure sufficient removal of the heat generated by the exothermic reaction in order to control the reaction. This problem is especially pronounced in continuous flow systems using fixed bed reactors. Moreover conversion and product selectivity in epoxidation reactions of olefins are highly susceptible to temperature changes with the effect that efficient temperature control is of uppermost importance.

[0005] In WO 97/47614 with reference to example 8 reaction of propene with hydrogen peroxide using a fixed bed tubular reactor having a cooling jacket in up-flow operation is described. But yield and product selectivity are still insufficient for commercial purposes.

[0006] Especially in highly exothermic reactions like epoxidation reactions effective removal of the heat of reaction is very important. When using fixed bed tubular reactors with cooling jacket like in WO 97/47614 it might become difficult to control heat generation within the catalyst packing inside the reactor. One possibility to overcome this problem is to use tube bundle reactors wherein the catalyst is either packed within the single tubes or outside the single tubes. To ensure uniform heat dissipation essential in exothermic reactions in the first case tube diameter has to be small and in latter case the distance between single tubes has to be small. Both possibilities create problems when designing the reactor. Operation of those tube bundle reactors having a high

number of single tubes is likewise difficult since these reactors are susceptible to blocking and fouling. Furthermore filling with catalyst to ensure uniform packing of the catalyst bed and exchange of deactivated catalyst for regeneration is becoming increasingly difficult with increased number of tubes or reduced distance between single tubes.

[0007] EP-A 659 473 describes an epoxidation process wherein a liquid mixture of hydrogen peroxide, solvent and propene is led over a succession of fixed bed reaction zones connected in series in down-flow operation. No temperature control means are present within the reactor to remove the generated heat from the single reaction zones. Thus each reaction zone can be considered as an independent adiabatic reactor. In each reaction zone the reaction is performed to a partial conversion, the liquid reaction mixture is removed from each reaction zone, is led over an external heat exchanger to extract the heat of reaction, and the major portion of this liquid phase is then recycled to this reaction zone and a minor portion of the liquid phase is passed to the next zone. At the same time gaseous propene is fed in together with the liquid feed stock mixture, is guided in a parallel stream to the liquid phase over the fixed bed reaction zones, and is extracted at the end of the reaction system in addition to the liquid reaction mixture as an oxygen-containing waste gas stream. Although this reaction procedure enables the propene oxide yield to be raised compared to conventional tubular reactors without the temperature control described in EP-A 659 473, it nevertheless involves considerable additional costs on account of the complexity of the reaction system required to carry out the process.

[0008] From US-A 5 849 937 a process for epoxidation of propene using hydroperoxides especially organic hydroperoxides is known. The reaction mixture is fed to a cascade of serially connected fixed bed reactors in down-flow regime with respect to each single reactor. Similarly to the teaching of EP-A 659 473 in each reactor only partial conversion is accomplished and the reactors are not equipped with heat exchange means. Like in EP-A 659 473 the reaction heat is removed by passing the effluent from each reactor through heat exchangers prior to introducing the reaction mixture to the next fixed bed reactor in series thereby adding to the complexity of the reaction system.

[0009] The disadvantages of the reaction systems as discussed in EP-A 659 473 and US-A 5 849 937 are the complexity and thus the increased costs for investment and the high susceptibility to changes of process parameters like flow velocity due to the adiabatically operated independent reaction zones and reactors respectively.

[0010] WO 99/29416 discloses a reactor for the catalytic reaction of gaseous reaction media having a plate heat exchanger whereby the catalyst bed is located between the heat exchange plates and the cooling medium or heating medium is passed counter currently to the gaseous reaction phase through the heat exchange

plates. There is neither reference to liquid phase or multiphase reaction media in general nor to oxidation or epoxidation reactions.

**[0011]** In view of the cited prior art the object of the present invention is to provide a process for the epoxidation of olefins that results in improved conversion and product selectivity compared to WO 97/47614 while avoiding the disadvantages of the teachings of EP-A 659 473 and US-A 5 849 937 which can be carried out using conventional reaction systems.

#### Subject of the Invention

**[0012]** This object is achieved by a process for the catalytic epoxidation of olefins with hydrogen peroxide in a continuous flow reaction system, wherein the reaction mixture comprising at least one liquid phase is passed through a fixed catalyst bed positioned between parallel heat exchange plates and the reaction heat is at least partially removed during the course of the reaction by passing a cooling medium through the heat exchange plates.

**[0013]** A particularly preferred embodiment of the present invention refers to a process for the catalytic epoxidation of propene with hydrogen peroxide in a continuous flow reaction system conducted in a multiphase reaction mixture comprising a liquid aqueous hydrogen peroxide rich phase containing methanol and a liquid organic propene rich phase, wherein the reaction mixture is passed through a fixed catalyst bed positioned between parallel heat exchange plates in down-flow operation mode and the reaction heat is at least partially removed during the course of the reaction by passing a cooling medium through the heat exchange plates.

**[0014]** The present inventors have surprisingly discovered, that by using a reactor with a bundle of parallel heat exchange plates wherein a fixed bed of catalyst is positioned between the heat exchange plates the epoxidation of olefins with hydrogen peroxide can be conducted with high olefin oxide selectivity at high hydrogen peroxide conversion compared to tubular reactors with a cooling jacket. Without wanted to be bound by theory it is believed that this surprising effect is attributed to a more uniform heat dissipation when using the reactor type of the present invention.

**[0015]** Compared to tube bundle reactors the dimensions of the plate bundle reactor to be used in the process of the present invention are considerably reduced at the same space-time yield. Thus investment costs are considerably lower. Furthermore the reactor to be used according to the present invention is less susceptible to blocking and fouling compared to tube bundle reactors.

**[0016]** Although WO 99/29416 describes some advantages of a reactor having parallel heat exchange plates it is not derivable from that prior art that especially in liquid phase or multiple phase exothermic reaction systems the selectivity at high conversion can be increased compared to reactor types that are commonly

used for example in epoxidation reactions.

#### Detailed Description of the Invention

**[0017]** In the practice of the present invention any reactor having a fixed catalyst bed positioned between parallel heat exchange plates can be used. Tubular reactors with parallel heat exchange means, whereby the distance between heat exchange plates is in the range of 0.5 to 50 mm, preferably 10 to 30 mm, are particularly preferred. Adiabatic reaction conditions as taught in EP-A 659 473 and US-A 5 849 937 should be avoided. As cooling medium that is pumped through the flow channels within the heat exchange plates all standard cooling media like oils, alcohols, liquid salts or water can be used. Water is most preferred. The cooling medium can be passed through the heat exchange plates counter-currently, co-currently or in cross-flow mode, whereby a cocurrent flow is most preferred.

**[0018]** In one preferred embodiment of the present invention the catalyst is packed between the heat exchange plates. Alternatively the catalyst is coated on the outside surface of the heat exchange plates. When using the alternative embodiment particularly small distances between heat exchange plates can be adjusted, thereby increasing the total heat exchange surface area at constant reactor dimensions.

**[0019]** The process according to the invention for the epoxidation of olefins, preferably propene, is typically carried out at a temperature of 30° to 80°C, preferably at 40° to 60°C. According to a preferred embodiment of the present invention the temperature profile within the reactor is maintained such that the cooling medium temperature of the cooling means is at least 40°C and the maximum temperature within the catalyst bed is 60°C at the most, preferably 55°C. By preference the temperature of the cooling medium is controlled by a thermostat.

**[0020]** The maximum temperature within the catalyst bed is measured with a plurality of suitable temperature measurement means like thermocouples or a Pt-100 arranged along the length of the reactor in suitable distances with respect to each other. Whereby number, position within the reactor and distances between the temperature measurement means are adjusted to measure the temperature of the catalyst bed within the entire reactor as exact as necessary.

**[0021]** The maximum temperature of the catalyst bed can be adjusted by different means. Depending on the selected reactor type the maximum temperature of the catalyst bed can be adjusted by controlling the flow rate of the reaction mixture passing through the reactor, by controlling the flow rate of the cooling medium passing through the cooling means or by lowering the catalyst activity, for instance by diluting the catalyst with inert material.

**[0022]** The flow rate of the cooling medium is preferably adjusted to keep the temperature difference be-

tween entry of the cooling medium into the cooling means and exit below 5°C, preferably below 3°C, most preferably 2°C..

**[0023]** By selecting such a narrowly defined temperature profile within the reactor an optimized balance between hydrogen peroxide conversion and olefin oxide selectivity can be achieved.

**[0024]** The pressure within the reactor is usually maintained at 5 to 50 bar preferably 15 to 30 bar.

Furthermore the present inventors realized that the combination of the reactor type used according to the present process and down-flow operation mode for the liquid reaction mixture results in surprisingly improved olefin selectivity at high hydrogen peroxide conversion.

**[0025]** In A. Gianetto, "Multiphase Reactors: Types, Characteristics and Uses", in Multiphase Chemical Reactors: Theory, Design, Scale-up, Hemisphere Publishing Corporation, 1986 criteria governing the choice between up-flow and down-flow fixed bed multiphase reactors are given. Advantages of up-flow regime compared to down-flow regime are:

- better mixing resulting in improved heat and mass transfer;
- at the same fluid flow rates the up-flow operation provides higher volumetric gas/liquid mass transfer coefficients;
- better liquid distribution in the cross section;
- better heat dissipation and more uniform temperature;
- better wetting of the catalyst and therefore increased catalyst effectiveness;
- slower aging of the catalyst
- avoiding compacting of the catalyst bed.

Disadvantages are:

- larger pressure drops and higher energy expenditure for pumping;
- reactor has to comprise means to hold the catalyst in place in case of high velocities;
- higher mass transfer resistance inside the liquid and an increase in possible homogeneous side reactions can occur.

**[0026]** In view of the advantages with respect to heat transfer and dissipation up-flow operation of a fixed bed reactor for multiphase reaction systems is the natural choice for highly exothermic reactions where temperature control is important.

**[0027]** Contrary to the general textbook knowledge as exemplified by A. Gianetto supra, the present inventors discovered that a cooled fixed bed reactor can be successfully operated in a down-flow operation to increase product selectivity and thereby overall product yield compared to an up-flow operation as previously used in the prior art. This effect is even more surprising since it is known that the epoxidation of olefin is a highly exo-

thermic reaction that is difficult to control since this reaction has a considerably high activation temperature and therefore has to be conducted at a certain minimum temperature to achieve economically reasonable conversion. But on the other hand the heat generated by the exothermic reaction has to be effectively removed from the reactor since at increased temperatures unwanted side reactions take place with the result that product selectivity is decreased. The effect of limited temperature increase within the catalyst bed is discussed to some extent in EP-A-659 473. With respect to the examples it is disclosed that in conventional tubular reactors temperature rise in the catalyst bed exceeds 15°C whereas according to the examples in EP-A-659 473 the temperature rise is 8°C at the most and in the preferred embodiment 5½°C. Thus according to the teaching of EP-A-659 473 temperature rise within the catalyst bed has to be kept as low as possible in order to achieve high yields of propylene oxide. This reduced temperature rise could only be achieved according to EP-A-659 473 by conducting the reaction in a single reaction zone to only a partial conversion with the result that the majority of the reaction mixture has to be recycled, and by intermediately cooling the reaction mixture.

**[0028]** According to the teaching of A. Gianetto et al. when operating a conventional tubular fixed bed reactor poor heat dissipation and nonuniform temperature within the catalyst bed has to be expected in case of down-flow operation mode. Thus it has to be expected that by using a downflow operation mode in a conventional cooled fixed bed reactor without intermediate external cooling of the reaction mixture a high temperature rise within the catalyst bed due to poor heat dissipation would occur that should dramatically decrease product selectivity and thus the yield. But contrary to this expectation using the process according to the present invention in down-flow operation mode leads to high olefin selectivity at high hydrogen peroxide conversion.

**[0029]** Another advantage of the reactor type to be used according to the present invention in down-flow operation mode of the reaction mixture compared to tube bundle reactors is that uniform feed of the liquid reaction mixture to the catalyst bed is much more easily to be accomplished. In tube bundle reactors especially those that contain the catalyst bed within the tubes means to supply the reaction mixture to each single tube have to be provided in down-flow operation to ensure uniform flow within the reactor resulting in very complicated and expensive equipment. In contrast thereto when using the plate bundle reactor according to the present invention the flow channels for the reaction mixture between the heat exchange plates are much larger in traverse direction so that the reaction mixture has to be supplied only to few locations along the width of one single flow channel to ensure uniform flow within the reactor. Furthermore standard equipment used for liquid distribution in distillation columns can be used to feed the reaction

mixture to the individual catalyst layers between the heat exchange plates. Preferably liquid distributors with tubes or channels parallel to the heat exchange plates and holes, slots or nozzles at regular intervals are used to supply the feed mixture. Such liquid distributors are known from K. Sattler, Thermische Trennverfahren, VCH Verlagsgesellschaft, 1995, table 2-35.

**[0030]** According to a preferred embodiment the reaction mixture is passed through the catalyst bed with a superficial velocity from 1 to 100 m/h, preferably 5 to 50 m/h, most preferred 5 to 30 m/h. The superficial velocity is defined as the ratio of volume flow rate/cross section of the catalyst bed. Consequently the superficial velocity can be varied in a given reactor by adjusting the flow rate of the reaction mixture.

**[0031]** Additionally it is preferred to pass the reaction mixture through the catalyst bed with a liquid hourly space velocity (LHSV) from 1 to 20 h<sup>-1</sup>, preferably 1.3 to 15 h<sup>-1</sup>.

**[0032]** Whenever the flow rate of the reaction mixture is adjusted to fulfill the above defined requirements for superficial velocity and liquid hourly space velocity particularly high selectivities can be achieved.

**[0033]** According to particularly preferred embodiment of the present invention the process is conducted to maintain the catalyst bed in a trickle bed state. It has been surprisingly discovered that if the trickle bed state is maintained under certain flow conditions the effect of the present invention i.e. the increased propene oxide selectivity will be particularly pronounced.

**[0034]** These conditions are as follows:

$$\begin{aligned} G/\lambda &< 2000 \text{ m/h and} \\ L\psi &< 50 \text{ m/h,} \end{aligned}$$

wherein

G is the gaseous superficial velocity defined as the gaseous flow rate in m<sup>3</sup>/h in the continuous flow reactor divided by the cross-section of the catalyst bed in m<sup>2</sup>,

L is the liquid superficial velocity defined as the liquid flow rate in m<sup>3</sup>/h in the continuous flow reactor divided by the cross-section of the catalyst bed in m<sup>2</sup>,

$$\lambda = \left[ \left( \frac{\rho_G}{\rho_W} \right) \left( \frac{\rho_L}{\rho_{Air}} \right) \right]^{1/2}$$

and

$$\psi = \left( \frac{\sigma_W}{\sigma_L} \right) \cdot \left[ \left( \frac{\mu_L}{\mu_W} \right) \left( \frac{\rho_W}{\rho_L} \right)^2 \right]^{1/3}$$

$\rho_G$  is the density of the gaseous phase in g/cm<sup>3</sup>,

$\rho_L$  is the density of the liquid phase in g/cm<sup>3</sup>,

$\rho_W$  is the density of water in g/cm<sup>3</sup>,

$\rho_{Air}$  is the density of air in g/cm<sup>3</sup>,

$\sigma_W$  is the surface tension of water in dyn/cm,

$\sigma_L$  is the surface tension of the liquid phase in dyn/cm,

$\mu_L$  is the viscosity of the liquid phase in centipoise,

$\mu_W$  is the viscosity of water in centipoise.

**[0035]** In order to be able to operate the process continuously when changing and/or regenerating the epoxidation catalyst, two or more flow reactors may if desired also be operated in parallel or in series in the before-described manner.

**[0036]** Crystalline, titanium-containing zeolites especially those of the composition (TiO<sub>2</sub>)<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> where x is from 0.001 to 0.05 and having a MFI or MEL crystalline structure, known as titanium silicalite-1 and titanium silicalite-2, are suitable as catalysts for the epoxidation process according to the invention. Such catalysts may be produced for example according to the process described in US-A 4,410,501. The titanium silicalite catalyst may be employed as a shaped catalyst in the form of granules, extrudates or shaped bodies. For the forming process the catalyst may contain 1 to 99% of a binder or carrier material, all binders and carrier materials being suitable that do not react with hydrogen peroxide or with the epoxide under the reaction conditions employed for the epoxidation. Extrudates with a diameter of 1 to 5 mm are preferably used as fixed bed catalysts.

**[0037]** When practicing the present invention it is preferred that the overall feed stream to the reactor comprises an aqueous hydrogen peroxide solution, an olefin and an organic solvent. Thereby these components may be introduced into the reactor as independent feeds or one or more of these feeds are mixed prior to introduction into the reactor.

**[0038]** Using the process according to the invention any olefins can be epoxidized in particular olefins with 2 to 6 carbon atoms. The process according to the invention is most particularly suitable for the epoxidation of propene to propene oxide. For economic reasons it would be preferred for an industrial scale process to use

propene not in a pure form but as a technical mixture with propane that as a rule contains 1 to 15 vol.% of propane. Propene may be fed as a liquid as well as in gaseous form into the reaction system.

**[0039]** The hydrogen peroxide is used in the process according to the invention in the form of an aqueous solution with a hydrogen peroxide content of 1 to 90 wt.%, preferably 10 to 70 wt.% and particularly preferably 30 to 50 wt.%. The hydrogen peroxide may be used in the form of the commercially available, stabilized solutions. Also suitable are unstabilized, aqueous hydrogen peroxide solutions such as are obtained in the anthraquinone process for producing hydrogen peroxide.

**[0040]** The reaction is preferably carried out in the presence of a solvent in order to increase the solubility of the olefin, preferably propene, in the liquid phase. Suitable as solvent are all solvents that are not oxidized or are oxidized only to a slight extent by hydrogen peroxide under the chosen reaction conditions, and that dissolve in an amount of more than 10 wt.% in water. Preferred are solvents that are completely miscible with water. Suitable solvents include alcohols such as methanol, ethanol or tert.-butanol; glycols such as for example ethylene glycol, 1,2-propanediol or 1,3-propanediol; cyclic ethers such as for example tetrahydrofuran, dioxane or propylene oxide; glycol ethers such as for example ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether or propylene glycol monomethyl ether, and ketones such as for example acetone or 2-butanone. Methanol is particularly preferably used as solvent.

**[0041]** The olefin is preferably employed in excess relative to the hydrogen peroxide in order to achieve a significant consumption of hydrogen peroxide, the molar ratio of olefin, preferably propene, to hydrogen peroxide preferably being chosen in the range from 1.1 to 30. The solvent is preferably added in a weight ratio of 0.5 to 20 relative to the amount of hydrogen peroxide solution used. The amount of catalyst employed may be varied within wide limits and is preferably chosen so that a hydrogen peroxide consumption of more than 90%, preferably more than 95%, is achieved within 1 minute to 5 hours under the employed reaction conditions.

**[0042]** According to one embodiment of the present invention reaction conditions like temperature, pressure, selection of olefin and selection of solvent and relative amounts of the components of the reaction mixture are chosen to ensure the presence of only one liquid phase wherein both the olefin and the hydrogen peroxide are dissolved. An additional gaseous olefin containing phase may also be present.

**[0043]** In another embodiment of the invention the epoxidation of olefins with hydrogen peroxide is conducted in a multiphase reaction mixture comprising a liquid aqueous hydrogen peroxide rich phase containing an organic solvent having a solubility in water of at least 10 % by weight at 25°C and a liquid organic olefin rich phase. Thereby an even better product selectivity can

be achieved.

**[0044]** As is appreciable by any person skilled in the art the presence of two immiscible liquid phases in a reaction system comprising an olefin, an water miscible organic solvent and an aqueous hydrogen peroxide solution will depend on many different factors. First of all the presence of an additional olefin rich liquid organic phase will depend on the temperature and pressure applied in the reactor and the selected olefin. Preferably the applied pressure is at or above the vapor pressure of the olefin at the chosen temperature. Furthermore it will depend on the selection of the organic solvent. Suitable as organic solvent are all solvents that dissolve in an amount of more than 10 wt.% in water at 25°C. Preferred are solvents that dissolve in an amount of more than 30 wt.% in water at 25°C preferably more than 50 wt.% in water at 25°C. The most preferred solvents are completely miscible with water. In principle all solvents as exemplified above can also be used in this preferred embodiment as long as the conditions are met to ensure the presence of two liquid phases.

**[0045]** Additionally the presence of a second organic olefin rich phase will depend on the relative amounts of olefin, water and solvent. The amount of solvent is chosen to achieve sufficient solubility of the olefin in the hydrogen peroxide rich aqueous phase in order to get the desired rate of reaction. At a given temperature, pressure, olefin and solvent the relative amounts of ingredients can be adjusted to ensure formation of a second liquid organic phase. I.e. to ensure the formation of a second liquid organic olefin rich phase the amount of olefin has to be selected in excess of the amount soluble in the aqueous phase at the chosen temperature and pressure.

**[0046]** A simple means of experimentally confirming the presence of a second liquid organic phase at the reaction conditions is by collecting a sample of the reaction mixture in a container equipped with a sight glass at the temperature and pressure used in the process. Alternatively, the reactor may be equipped with a sight glass at a suitable position to observe the phase boundary directly during the reaction. In case of a continuous flow reactor the sight glass is preferably positioned near the outlet of the reactor effluent to have an optimal control that two liquid phases are present throughout the entire residence time within the reactor.

**[0047]** Thus a person skilled in the art can without any effort verify whether when applying certain selections for olefins, solvents and reaction parameters a two-liquid phase system as required by the present invention is present and can adjust by variation of the parameters as discussed above in detail the reaction system in order to establish a second liquid organic phase.

**[0048]** According to a most preferred embodiment of the present invention the olefin is selected to be propene, and methanol is used as a solvent. For example for a reaction mixture comprising propene, methanol, and aqueous hydrogen peroxide at a reaction tempera-

ture between 30°C and 80°C, a pressure from 5 to 50 bar the ratio of propene flow to total flow in case of a continuous flow system can be adjusted to be in the range of 0.1 to 1, preferably 0.2 to 1 in order to obtain a second liquid organic phase.

[0049] An additional gas phase comprising olefin vapor and optionally an inert gas i.e. a gas that does not interfere with the epoxidation can be additionally present according to the present invention. Adding an inert gas is useful to maintain a constant pressure inside the reactor and to remove oxygen gas formed by the decomposition of a small part of the hydrogen peroxide charged to the reactor.

#### Claims

1. A process for the catalytic epoxidation of olefins with hydrogen peroxide in a continuous flow reaction system, wherein the reaction mixture comprising at least one liquid phase is passed through a fixed catalyst bed positioned between parallel heat exchange plates and the reaction heat is at least partially removed during the course of the reaction by passing a cooling medium through the heat exchange plates.
2. The process of claim 1, wherein the heat exchange plates are positioned within a tubular reactor and the distance between heat exchange plates is in the range of 0.5 to 50 mm, preferably 10 to 30 mm.
3. The process of any of claims 1 and 2, wherein the catalyst is packed between the heat exchange plates.
4. The process of any of claims 1 and 2, wherein the catalyst is coated on the outside surface of the heat exchange plates.
5. The process of any of the preceding claims, wherein the reaction mixture is passed through the catalyst bed with a superficial velocity from 1 to 100 m/h, preferably 5 to 50 m/h, most preferably 5 to 30 m/h.
6. The process of any of the preceding claims, wherein the reaction mixture is passed through the catalyst bed with a liquid hourly space velocity (LHSV) from 1 to 20 h<sup>-1</sup>, preferably 1.3 to 15 h<sup>-1</sup>.
7. The process of any of the preceding claims, wherein the reaction mixture is passed through the catalyst bed in down-flow operation mode.
8. The process of claim 7, wherein the fixed catalyst bed is maintained in a trickle bed state.
9. The process of claim 8, wherein trickle bed state is

maintained under following flow conditions:

$$G/\lambda < 2000 \text{ m/h and} \\ L/\lambda < 50 \text{ m/h,}$$

wherein

G is the gaseous superficial velocity defined as the gaseous flow rate in m<sup>3</sup>/h in the continuous flow reaction system divided by the cross-section of the catalyst bed in m<sup>2</sup>,

L is the liquid superficial velocity defined as the liquid flow rate in m<sup>3</sup>/h in the continuous flow reaction system divided by the cross-section of the catalyst bed in m<sup>2</sup>,

$$\lambda = \left[ \left( \frac{\rho_G}{\rho_W} \right) \left( \frac{\rho_L}{\rho_{Air}} \right) \right]^{1/2}$$

,and

$$\psi = \left( \frac{\sigma_W}{\sigma_L} \right) \cdot \left[ \left( \frac{\mu_L}{\mu_W} \right) \left( \frac{\rho_W}{\rho_L} \right)^2 \right]^{1/3}$$

$\rho_G$  is the density of the gaseous phase in g/cm<sup>3</sup>,

$\rho_L$  is the density of the liquid phase in g/cm<sup>3</sup>,

$\rho_W$  is the density of water in g/cm<sup>3</sup>,

$\rho_{Air}$  is the density of air in g/cm<sup>3</sup>,

$\sigma_W$  is the surface tension of water in dyn/cm,

$\sigma_L$  is the surface tension of the liquid phase in dyn/cm,

$\mu_L$  is the viscosity of the liquid phase in centipoise,

$\mu_W$  is the viscosity of water in centipoise.

10. The process of any of claims 7-9, wherein distribution means selected from tubes or channels parallel to the heat exchange plates and holes, slots or nozzles at regular intervals are used to feed the reaction mixture to the individual catalyst layers between the heat exchange plates.

11. The process of any of the preceding claims, wherein the reaction temperature is from 30 to 80°C, preferably from 40 to 60°C.
12. The process of claim 11, wherein a temperature profile within the reactor is maintained such that the cooling medium temperature of the cooling means is at least 40°C and the maximum temperature within the catalyst bed is 60°C at the most. 5
13. The process of any of the preceding claims, wherein the pressure within the reactor is maintained at 5 to 50 bar, preferably at 15 to 30 bar. 10
14. The process of any of the preceding claims, wherein the overall feed stream to the reactor comprises an aqueous hydrogen peroxide solution, an olefin and an organic solvent. 15
15. The process of claim 14, wherein the reaction is conducted in a multiphase reaction mixture comprising an liquid aqueous hydrogen peroxide rich phase containing an organic solvent having a solubility in water of at least 10 % by weight at 25°C and an liquid organic olefin rich phase. 20 25
16. The process of any of the claims 14 and 15, wherein the organic solvent is methanol.
17. The process of any of the preceding claims, wherein a titanium-containing zeolite is used as catalyst. 30
18. The process of any of the preceding claims, wherein the olefin is propene. 35
19. A process for the catalytic epoxidation of propene with hydrogen peroxide in a continuous flow reaction system wherein a reaction mixture comprising hydrogen peroxide, methanol and propene is passed through a fixed catalyst bed positioned between parallel heat exchange plates in down-flow operation mode and the reaction heat is at least partially removed during the course of the reaction by passing a cooling medium through the heat exchange plates. 40 45
20. The process of claim 19, wherein the reaction mixture is a multiphase reaction mixture comprising an liquid aqueous hydrogen peroxide rich phase containing methanol and a liquid organic propene rich phase. 50

55





**European Patent  
Office**

## EUROPEAN SEARCH REPORT

Application Number  
EP 01 11 9565

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	DE 196 23 611 A (BASF AG) 18 December 1997 (1997-12-18) * column 3, line 42-54 * * example 8 * * claim 1 *	1-18	C07D301/12
D,Y	US 5 849 937 A (JUBIN JR JOHN C ET AL) 15 December 1998 (1998-12-15) * figure 2 * * claims 1,22 *	1-18	
D,Y	EP 0 659 473 A (ARCO CHEM TECH) 28 June 1995 (1995-06-28) * page 1, line 6-24 * * claim 1 *	1-18	
D,Y	DE 197 54 185 C (DEG ENGINEERING GMBH) 4 February 1999 (1999-02-04) * page 1, line 1-3,14-17 * * figures 1-3 * * claim 1 *	1-18	
A	US 2 870 171 A (GABLE CHARLES M) 20 January 1959 (1959-01-20) * claim 1 *	1-18	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C07D
A	US 5 523 426 A (JUBIN JR JOHN C ET AL) 4 June 1996 (1996-06-04) * claim 1 *	1-18	
A	EP 0 568 337 A (ARCO CHEM TECH) 3 November 1993 (1993-11-03) * claim 1 *	1-18	
A	US 5 912 367 A (CHANG TE) 15 June 1999 (1999-06-15) * claim 1 *	1-18	
<p style="text-align: center;">-/-</p> <p style="text-align: center;">-/-</p>			
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>10 January 2002</b>	Examiner <b>Samsam Bakhtiary, M</b>
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p> X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document </p>	



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 01 11 9565

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 5 760 253 A (JUBIN JR JOHN C ET AL) 2 June 1998 (1998-06-02) * claim 1 *	1-18	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
-The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 10 January 2002	Examiner Samsam Bakhtiary, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P04C01)

# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 01 11 9565

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-01-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 19623611	A	18-12-1997	DE 19623611 A1	18-12-1997
			AU 3093297 A	07-01-1998
			WO 9747614 A1	18-12-1997
US 5849937	A	15-12-1998	AU 1026099 A	12-07-1999
			BR 9813834 A	21-11-2000
			CA 2310427 A1	01-07-1999
			CN 1282328 T	31-01-2001
			WO 9932472 A1	01-07-1999
			EP 1047681 A1	02-11-2000
			JP 2001526280 T	18-12-2001
EP 0659473	A	28-06-1995	US 5466836 A	14-11-1995
			AT 171394 T	15-10-1998
			CA 2137310 A1	21-06-1995
			CN 1109382 A	04-10-1995
			DE 69413507 D1	29-10-1998
			DE 69413507 T2	11-02-1999
			EP 0659473 A1	28-06-1995
			ES 2121162 T3	16-11-1998
			JP 7196639 A	01-08-1995
			RU 2126799 C1	27-02-1999
			US 5468885 A	21-11-1995
			US 5573736 A	12-11-1996
DE 19754185	C	04-02-1999	DE 19754185 C1	04-02-1999
			WO 9929416 A1	17-06-1999
			EP 0963247 A1	15-12-1999
US 2870171	A	20-01-1959	NONE	
US 5523426	A	04-06-1996	AT 165353 T	15-05-1998
			CA 2166425 A1	05-07-1996
			CN 1134937 A ,B	06-11-1996
			DE 69600245 D1	28-05-1998
			DE 69600245 T2	13-08-1998
			EP 0720984 A1	10-07-1996
			ES 2115414 T3	16-06-1998
			JP 8245603 A	24-09-1996
			RU 2162466 C2	27-01-2001
			SG 34364 A1	06-12-1996
			TW 397830 B	11-07-2000
EP 0568337	A	03-11-1993	US 5214168 A	25-05-1993
			EP 0568337 A2	03-11-1993
			JP 6009593 A	18-01-1994

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 9565

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-01-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5912367	A	15-06-1999	AU 8730598 A	25-01-1999
			BR 9810377 A	05-09-2000
			CN 1261359 T	26-07-2000
			WO 9901445 A1	14-01-1999
			EP 1190770 A1	27-03-2002
			EP 0993453 A1	19-04-2000
			JP 2002508779 T	19-03-2002
			US 6066750 A	23-05-2000
US 5760253	A	02-06-1998	AU 6616298 A	18-08-1998
			BR 9806981 A	14-03-2000
			CN 1244816 T	16-02-2000
			DE 69803082 D1	31-01-2002
			WO 9832530 A1	30-07-1998
			EP 1017487 A1	12-07-2000
			ES 2165148 T3	01-03-2002
			JP 2002509530 T	26-03-2002

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82